

# PATENT ABSTRACTS OF JAPAN

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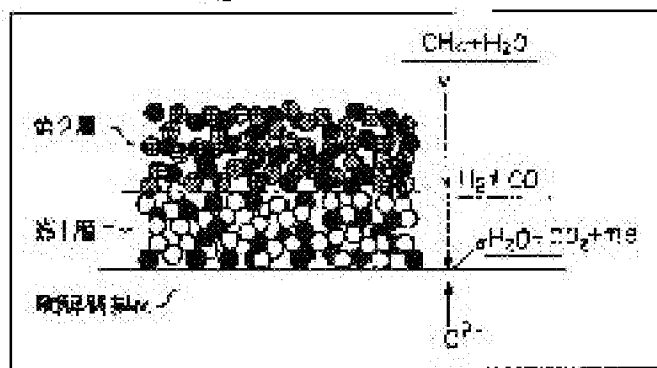
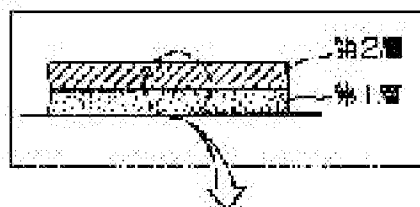
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## (54) FUEL ELECTRODE FOR SOLID ELETROLYTE FUEL CELL

(57)Abstract:

**PURPOSE:** To prevent degradation of fuel cell performance by forming two porous electrode layers of both an Ni+YSZ constitution and a Ni+basic aggregate constitution on the surface of an electrolytic base material.

**CONSTITUTION:** The first porous electrode layer of an Ni+YSZ constitution and the second porous electrode layer of an Ni+basic aggregate constitution are formed on the surface of an electrolyte base material. An electrode reaction function is given to the first layer, and a reforming catalyst function of carbon proof deposition property is given to the second layer, and hydrocarbon is prevented from coming into contact directly with the first layer by adopting an electrode structure, and electrode reaction is highly activated between quasi reforming hydrogen and oxygen ion, so that degradation of fuel cell performance can be prevented.



● : Ni+YSZ, ○ : Ni+basic aggregate

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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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## CLAIM + DETAILED DESCRIPTION

### [Claim(s)]

[Claim 1] The 1st porous electrode layer containing yttria-stabilized-zirconia aggregate, a nickel metal, or its oxide grain is formed in the surface of a solid electrolyte base material. The fuel electrode of the solid oxide fuel cell characterized by furthermore forming the 2nd porous electrode layer containing basic aggregate, a nickel metal, or its oxide grain in the surface.

[Claim 2] As basic aggregate which constitutes the porous electrode layer of the above 2nd, it is MgAl<sub>2</sub>O<sub>4</sub>, CaAl<sub>2</sub>O<sub>4</sub>, MgO and 2TiO<sub>2</sub>, and MgO-ZrO<sub>2</sub>. And CeO<sub>2</sub> Fuel electrode of the solid oxide fuel cell according to claim 1 characterized by using one or more sorts of aggregate chosen from a group.

### [Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the fuel electrode of the solid oxide fuel cell for high temperature (Solid Oxide Fuel Cells, Following SOFC and a brief sketch) which uses coal gasification gas and natural gas as a primary fuel about the fuel electrode of a fuel cell.

[0002]

[Description of the Prior Art] As SOFC was illustrated to drawing 12, on both sides of the solid electrolyte material 2, the air electrode 1 and the fuel electrode 4 are attached. In addition, 3 is tabular [ of porosity / 5 / a middle connection binder (interconnector) and ], or a tubular base. The solid electrolyte material 2 is 8mol% of Y<sub>2</sub>O<sub>3</sub> which has oxygen ion conductivity. The stabilized zirconia (it omits Following YSZ) which dissolved is used abundantly. The cermet which mixed YSZ with nickel when the PEROPUSUKAITO type multiple oxide which has stable and high conductivity also in the oxidizing atmosphere of high temperature [ electrode / 1 / air ] planned nickel or thermal adjustment with YSZ to the fuel electrode 4 again is used. To the middle connection binder 3, a La-Cr system PEROPUSUKAITO type oxide is still more typical. This cell is operated at about 1000 degrees C, and air or oxygen is supplied to the air pole side, and it supplies hydrogen to the fuel electrode side.

[0003] Although the fuel supplied to a fuel cell is mainly hydrogen, the hydrogen manufactured by steam reforming of coal gasification gas, natural gas, and naphtha is used with large-scale-izing of a cell. There is two kinds of form in hydrogen manufacturing methods, such as the latter natural gas, and there are an external property modification method which reforms out of a fuel cell subsystem and supplies

hydrogen, and an internal property modification method which reforms directly and is generated within a fuel cell subsystem in them. An internal property modification method is the system which fitted the fuel cell for high temperature especially, and there are the following features.

(1) Efficient-izing of the cell cooling load capability reduction (4) power-generation plant by the endotherm effect of the efficient-ized (3) reforming reaction of hydrogen manufacture of having used the miniaturization (2) cell heat source of the plant (comparing with external property modification) [0004] By the way, the fuel electrode room used as the fuel pass of a fuel cell mainly consists of connection material, such as a fuel electrode and an interconnector. Among these, fuel electrode material consists of cermet of YSZ aggregate and a Ni metal, when planning adjustment of a coefficient of thermal expansion with an electrolyte (YSZ), and generally the nickel presentation is 30 - 50 vol% of a range. Although the fuel electrode material of the fuel cell which consists of combination of nickel and YSZ is well-known, the other real example does not have now.

[0005]

[Problem to be solved by the invention] All the cell reactions of a fuel cell advance as follows through movement of the oxygen ion in an electrolyte.

Oxygen pole :  $O_2(g) + 2e^- = O^{2-}$  fuel electrode :  $H_2(g) + O^{2-} = H_2O + 2e^-$  overall reaction :  $H_2(g) + O_2(g) = H_2O(g)$

(Here, as for e, an electron and (g) show gas.)

The active substances of a cell are hydrogen and oxygen. Since the oxygen pole side can use oxygen in the air, it does not have a problem in particular. If the fuel electrode side also supplies the pure water matter refined by the aforementioned hydrogen manufacturing method, there will be no problem in particular.

[0006] the impurity contained in the fuel hydrogen when practical use fuels, such as coal gasification gas and natural gas, or town gas, are directly used with large-scale-izing of a fuel cell, for example,  $CH_4$ , etc. -- there is a problem that a light hydrocarbon and  $SO_x$  carry out poisoning of the fuel electrode material. [ however, ] It is remains  $CH_4$  which is the principal component especially when reforming hydrocarbons, such as natural gas, directly within a fuel cell subsystem with an internal property modification method and generating electricity. Fuel electrode material is deteriorated. This is the factors with a main carbon deposit in a fuel electrode.

[0007]  $CH_4$  etc. -- [ the steam-reforming catalyst of a light hydrocarbon ]  $\alpha$ -alumina ( $Al_2O_3$ ) of a former heat-resisting property nickel catalyst which made the carrier cordierite ( $2MgO$ ,  $2Al_2O_3$ , and  $5SiO_2$ ) etc. is well-known. Moreover, what added alkali alkaline earth metals and Ru metals, such as basic  $K_2O$  and  $MgO$ , as a measure against a carbon-proof deposit is used for this as an industrial practical use catalyst. As other measures against a carbon-proof deposit, thermodynamic operation on operation of what is called the increase in quantity of a S/C ratio (steam / carbon molar ratio), increase in quantity of  $CO_2 / C$  ratio, etc. which makes the amount of supply steam more superfluous than a stoichiometry ratio is performed.

[0008] Although the Ni metal which is the above-mentioned catalytic activity component is used for fuel electrode material in respect of a property modification function and there is no problem in particular, it is comparatively easy to generate carbon and the case of a fuel cell also has the problem of having the serious influence for the life of a fuel cell, when using acid YSZ for aggregate equivalent to catalyst support. There are the following problems in the measure against a carbon-proof deposit in the conventional fuel cell, and quite severe restrictions will be received in the measure.

- (1) Thermal adjustment can be planned in neither the conventional catalyst support nor introduction of an additive.
- (2) Neither the above-mentioned carrier nor the additive can bear hot environments of 1000 degrees C or more, but generates an impure product according to a solid phase reaction with neighboring group material.
- (3) Increase of a S/C ratio causes the thermal efficiency and loss of power of a cell due to latent heat loss of superfluous steam, and the fall of the active material concentration of a cell.
- [0009] So, when large-scale-izing a fuel cell, it is necessary about the fuel electrode material for internal property modification to lecture on the following deterioration preventive measures especially.
- (1) high-activity-izing of neighboring group material, the adjustment of a coefficient of thermal expansion with an electrolyte (YSZ) and thermal stability (2) neighboring-group material especially YSZ, INTAKONEKUTA, and a solid phase reaction-proof nature (3) high current collection functionality (4) steam-reforming catalyst with nickel, and carbon-proof deposit nature (5) low S/C -- a ratio ---izing (->1-2)

(6) Highly-efficient-izing of fuel electrode performance (reduction-izing of an overvoltage)

[0010] This invention persons are  $\text{MgAl}_2\text{O}_4$  of basicity [ that it is low-thermal-expansion nature as a measure against the preceding clause and ] in the Tokuganhei3-41855 application.  $\text{CaAl}_2\text{O}_4$  The electrode material of the fuel cell containing a spinel compound was proposed. [ namely, the fuel electrode material which consists of combination of Ni-metal grains and the above-mentioned basic aggregate ] Since frame material is low thermal expansion from YSZ, it is possible for the coefficient of thermal expansion ( $13.9 \times 10^{-6}$  degree-C<sup>-1</sup>) of NiO (generally it is a nickel oxide at the time of electrode manufacture) to be offset, and to double with the coefficient of thermal expansion of Electrolyte YSZ. Moreover, since the above-mentioned spinel compound is basicity, it is excellent in carbon-proof deposit nature, and can maintain the steam-reforming catalytic activity and the electrochemical catalysis where the low S/C ratio was also stabilized. Moreover, in the Tokuganhei2-238999 application, it is  $\text{CeO}_2$  as electrode aggregate. The same electrode material as the used above was proposed. This also has the same effect as the above.

[0011] However, important knowledge was acquired in the process which advances the electrode quality assessment in the above-mentioned electrode aggregate. That is, although the electrode material by the conventional Ni metal and the combination of YSZ aggregate acts very effective in the fuel electrode process ( $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ ) which is the elementary step of a cell reaction, the electrode performance of the above-mentioned aggregate other than YSZ, especially aggregate almost near insulation has the tendency to be inferior to a little conventional performance. Then, this invention tends to offer the fuel electrode of a hard electrolyte type fuel cell which holds the conventional electrode performance and satisfies the requirements for deterioration-proof nature of the preceding clause.

[0012]

[Means for solving problem] This invention forms the 1st porous electrode layer containing yttria-stabilized-zirconia aggregate, a nickel metal, or its oxide grain in the surface of a solid electrolyte base material. It is the fuel electrode of the solid oxide fuel cell characterized by furthermore forming the 2nd porous electrode layer containing basic aggregate, a nickel metal, or its oxide grain in the surface.

[0013] This invention persons are  $\text{MgO}$  and  $2\text{TiO}_2$  which is equivalent to the coefficient of thermal expansion of YSZ when it inquires about the electrode aggregate which satisfies the requirements for the above-mentioned deterioration preventive measures based on the above-mentioned knowledge.  $\text{MgO}$ -

ZrO<sub>2</sub> The multiple oxide also found out that it was effective as basic aggregate. Therefore, as basic aggregate which constitutes the 2nd porous electrode layer of the fuel electrode of this invention, it is MgAl<sub>2</sub>O<sub>4</sub>, CaAl<sub>2</sub>O<sub>4</sub>, MgO and 2TiO<sub>2</sub>, and MgO-ZrO<sub>2</sub>. And CeO<sub>2</sub> One or more sorts of aggregate chosen from a group can be used.

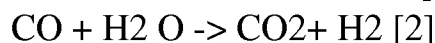
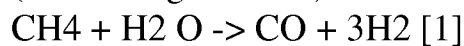
[0014]

[Function] Drawing 1 is the key map having expanded and shown the section of the fuel electrode which is one example of this invention. This fuel electrode The 1st porous electrode layer of composition (nickel+YSZ) on the surface of an electrolyte base material, (nickel+ basicity aggregate) by forming the 2nd porous electrode layer of composition, giving an electrode process function to the 1st porous electrode layer, and giving the property modification catalyst function of carbon-proof deposit nature to the 2nd porous electrode layer, and adopting the above-mentioned electrode structure It prevents contacting the 1st porous electrode layer directly, and a hydrocarbon high-activity-izes the electrode process of semi- property modification hydrogen and oxygen ion, and can prevent deterioration of fuel electrode performance and also fuel cell performance.

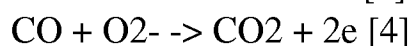
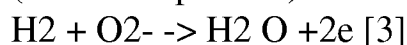
[0015] By being equivalent to the coefficient of thermal expansion (10x10<sup>-6</sup> degree-C<sup>-1</sup>) of Electrolyte YSZ, or adopting fuel electrode aggregate of low thermal expansion from this in this invention It becomes possible to be able to make this contain NiO the same range as usual, or more, and to, fully double a coefficient of thermal expansion with an electrolyte as a result, and most loads by thermal stress cannot be found. Moreover, at the temperature of 1000-1500 degrees C or more, the impure deposit by a solid phase reaction with neighboring group material is not accepted, either, and it does not become a problem from the place which is a stable electrode material also thermochemically at all on the fuel cell manufacture which needs high temperature heat treatment. Since the Ni metal used as an electric conduction medium is contained the former, equivalent quantity, or more, current collection nature has good metal conductivity. So, the material property of the fuel electrode of this invention being almost equivalent to the former or it is excelled, and there is no trouble in particular on the design of a fuel cell.

[0016] Maintenance of highly-efficient-izing of the carbon-proof deposit nature in the internal reforming reaction at the time of low S/C ratio operation which is described below, and a fuel electrode has the most characteristic operation of this invention. The internal reforming reaction of a fuel cell advances as the following in the fuel electrode interior of a room. In addition, it is a primary fuel here CH<sub>4</sub> Although carried out, also in a with a carbon numbers of two or more hydrocarbon, the last reaction process becomes the same.

(Reforming reaction)



(Electrode process)



[0017] In such an internal reforming reaction of a fuel cell, it is the consecutive reaction of the reforming reaction of [1] and [2], and the electrode process of [3] and [4], and a change does not have [1] or [2] reaction in any way with the usual steam reforming reaction fundamentally. Therefore, carbon generation was the same as that of the mechanism produced on a general property modification catalyst, and only transposed this to the fuel electrode. About the main development mechanism, it is based on

catalytic cracking of a hydrocarbon, and the disproportionation of CO. At 1000-degree C high temperature, catalytic cracking of a hydrocarbon happens especially easiliest. This catalytic cracking happens as a result of the dehydrogenation process of  $\text{CH}_x$  which strong-adsorbed mainly on the Ni-metal surface. Since it excels in the reactivity of steam and shifts to the property modification of the above [1] so that the value ( $<4$ ) of X of adsorption species  $\text{CH}_x$  is large, carbon is not generated, but if the value of X is small, it will become easy to generate carbon. Furthermore, if acid aggregate like YSZ adjoins the Ni metal, the carbon generation process will be promoted increasingly. However, like this invention, if basic aggregate is introduced, the dehydrogenation of  $\text{CH}_x$  will be eased, it will be urged to activation with steam, and, as a result, carbonaceous generation will be controlled by the electron release operation to a Ni metal from basic aggregate.

[0018] On the other hand, especially a fuel electrode process is governed by the reaction of [3] among [3] and [4]. As for the labile site, it is desirable to be near a gaseous phase / the nickel/YSZ 3 phase interface, therefore for the distance of this 3 phase interface to exist in both an electrode / electrolyte and an electrode thickness direction. This shows that the electrode material by the conventional Ni metal and the combination of YSZ aggregate is very effective in an electrode process. When the electrode material by this invention is used independently, the labile site will be restricted to the two-dimensional field of an electrode / electrolyte interface, and a labile point will decrease considerably conventionally. For this reason, also to an electrode thickness direction, only as for the thickness direction which acts effective in an electrode process, naturally it is advantageous to secure the distance of a 3 phase interface, and it can maintain electrode performance as usual.

[0019] [ the fuel electrode of this invention ] thus, by forming the 2nd porous electrode layer which has the property modification catalyst function of carbon-proof deposit nature on the 1st porous electrode layer which has an electrode process function A hydrocarbon cannot contact the 1st porous electrode layer, can make the electrode process in this layer high-activity-ize, and can prevent deterioration of a fuel electrode.

[0020]

[Working example] (Manufacture of a fuel electrode) An example of the method of preparation of the fuel electrode material with which the following work examples were presented is described below. As a starting material, it is YSZ (8 mol% $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$ ),  $\text{MgAl}_2\text{O}_4$ ,  $\text{CaAl}_2\text{O}_4$ ,  $\text{MgO}$  and  $2\text{TiO}_2$ , and  $\text{MgO-ZrO}_2$  to NiO and electrode aggregate in nickel raw material. Fine particles were used. These raw material grain sizes are 0.1-2-micrometer ranges in general. In addition,  $\text{MgO-ZrO}_2$  It is a solid solution and the amount of dissolution of MgO was made into a maximum of 20 mol%. First, specified quantity combination was carried out, distributed mixing of the precursor powder of NiO and each aggregate and the dispersant of the Pori acrylic was carried out with the wet ball mill, and homogeneous slurry was obtained.

[0021] In order to evaluate material physical properties, the slurry was fully dried, the classification was carried out to 100-150 micrometers or less, and predetermined time sintering of what added the organic binder to this was carried out at 1300-1400 degrees C after powder-compacting molding (or CIP: Cold Isostatic Press). The sintered compact controlled the porosity rate and the diameter of pore to the porous body of 1 micrometer or less 10 to 20%, respectively by changing the amount of binder addition, a raw material grain size and sintering temperature, and time to be able to imitate the organization of a porous electrode. hydrogen and  $\text{CH}_4$  etc. -- in combustion gas atmosphere, since NiO was returned, the final porosity rate and the final diameter of pore of the sintered compact increased to 1-2 micrometers 20 to

30%, respectively. [ in addition, ] This is the same also at the time of electrode manufacture. As physical properties of each electrode material, this example was estimating electric conductivity and a coefficient of thermal expansion, and the specimen at that time used what processed said sintered compact into the rectangular parallelepiped (3x3x15mm) by it.

[0022] Manufacture of the fuel electrode was based on the following process after said mixed end. First, vacuum defoaming treatment was carried out and previous mixed slurry was adjusted to proper slurry viscosity, after carrying out specified quantity addition of an organic binder and the plasticizer and mixing with a ball mill again. By the doctor blade method, this was fabricated in the shape of a sheet, and was dried. The green sheet after desiccation was stuck to the green sheet (100 micrometers) of YSZ prepared beforehand by pressure, and the fuel electrode was obtained by sintering at 1300-1400 degrees C for about 2 to 3 hours. Manufacture of the electrode two-layer structure concerning this invention was obtained by sticking the sheet of NiO+YSZ to a YSZ sheet by pressure first among the green sheets of each above-mentioned fuel electrode, then sticking the sheet of NiO+ each basic aggregate by pressure on the nickel+YSZ sheet, and sintering like the above. In addition, the same electrode two-layer structure can be manufactured by applying slurry of nickel+ basicity aggregate to the electrode surface directly, and sintering it to it besides the above-mentioned manufacturing method, after manufacturing a nickel+YSZ electrode beforehand. Thus, the thickness of the obtained final lamina electrode is about 100 micrometers, and a nickel+YSZ electrode layer is [ 50 micrometers and nickel+ basicity aggregate electrode layer of the thickness of the electrode two-layer structure ] 100 micrometers in total in 50 micrometers. In addition, if nickel+ basicity aggregate layer is not much thinner than this, deterioration of a nickel+YSZ electrode layer will be influenced. Moreover, if a nickel+YSZ electrode layer is also not much thinner than this, since electrode performance will fall, it needs to be careful. All serve as 20 to 30% of a porosity rate, and about 1-2 micrometers of diameters of pore by returning the porosity rate and the diameter of pore of each electrode like the above-mentioned sintered compact.

[0023] (The coefficient of thermal expansion of a fuel electrode material, and measurement of electric conductivity) The coefficient of thermal expansion and electric conductivity of a fuel electrode material are first shown in Table 1. A coefficient of thermal expansion is a temperature coefficient of the coefficient of thermal expansion for 20-1000 degrees C or 1100 degrees C. The coefficient of thermal expansion of YSZ which is an electrolyte at that time is  $10 \times 10^{-6}$  degree-C<sup>-1</sup>, and it turns out that all serve as a value almost near the coefficient of thermal expansion. [ since aggregate itself was an electrolyte, the conventional nickel+YSZ system aggregate layer had the dilemma of producing the difference of a coefficient of thermal expansion increasingly rather than the written coefficient of thermal expansion, when NiO (or nickel) was superfluously introduced from a viewpoint of high conductivity, but ] MgAl<sub>2</sub>O<sub>4</sub> CaAl<sub>2</sub>O<sub>4</sub> Since it is low-thermal-expansion material, even if it introduces NiO (or nickel) still more superfluous than before, a coefficient of thermal expansion with YSZ of a base material can be coincided.

[0024] On the other hand, electric conductivity is 1000 degrees C and H<sub>2</sub> by a direct-current four probe method. It is the value measured in the air current. The point which electric conductivity also increases so that there are many amounts of nickel, although it is natural, but should be noted is MgAl<sub>2</sub>O<sub>4</sub>. CaAl<sub>2</sub>O<sub>4</sub> It is the Ni content which sets and whose coefficient of thermal expansion with YSZ corresponds, and is that the electric conductivity of 1000 or more S/cm is obtained. Thus, MgAl<sub>2</sub>O<sub>4</sub> CaAl<sub>2</sub>O<sub>4</sub> By using for aggregate of a fuel electrode, coincidence of a coefficient of thermal expansion with the conventionally impossible YSZ base material and high electric conductivity were able to be reconciled.

MgO and  $2\text{TiO}_2$  of others, MgO-ZrO<sub>2</sub>, and CeO<sub>2</sub> etc. -- although a fuel electrode material also differs in some constraints by the thickness of each component, the manufacture scale, i.e., the cell area, of a fuel cell, it shows the convenient physical-properties value on cell manufacture in the nickel content range of Table 1 in general. [ moreover, ]

[0025]

[Table 1]

塩 基 性 骨 材	N i 組成範囲 ( vol%)	熱膨張係数 ( $10^{-6} \text{ }^{\circ}\text{C}^{-1}$ )	導 電 率 (S/cm)
MgAl <sub>2</sub> O <sub>4</sub>	35～60	10～12	1000～2500
CaAl <sub>2</sub> O <sub>4</sub>	35～60	10～12	1000～2500
MgO・2TiO <sub>2</sub>	20～45	11～12	0.1～2500
MgO・ZrO <sub>2</sub>	20～45	11～12	0.1～2500
CeO <sub>2</sub>	20～25	12	300～600
YSZ (比較材)	20～45	11～12	0.1～2500

[0026] (Composition of an electrode) The following work examples examined the result of Table 1 about the presentation typical about each electrode material to reference further. The Ni content at that time is shown in Table 2. In addition, CaAl<sub>2</sub>O<sub>4</sub> MgAl<sub>2</sub>O<sub>4</sub> There is no difference in material or an electrode characteristic in particular, and, also crystallographically, it omitted here for the same kind. About a two-layer structure electrode, it is MgAl<sub>2</sub>O<sub>4</sub> insulating, and MgO and  $2\text{TiO}_2$  insulating. Since there was especially an effect, it was shown as a work example.

[0027]

[Table 2]



サンプル記号	骨 材	N i 含有量 ( vol%)
a	Y S Z (比較材)	3 5
b	M g A l <sub>2</sub> O <sub>4</sub>	3 5
c	M g ・ 2 T i O <sub>2</sub>	3 5
d	M g ・ Z r O <sub>2</sub>	3 5
e	C e O <sub>2</sub>	3 5
f	b / a (二層構造)	3 5 / 3 5
g	c / a (二層構造)	3 5 / 3 5
h	d / a (二層構造)	3 5 / 3 5
i	e / a (二層構造)	3 5 / 3 5

[0028] (Carbon-proof deposit nature examination) The relation between the reaction temperature in the steam reforming reaction of methane and the amount of carbon deposits (the amount of deposits per unit catalyst weight) was shown in drawing 2 . The reaction condition is S/C=1 and GHSV(space velocity) =14900h<sup>-1</sup>, and reaction time is 20h. Although S/C=1 is generally conditions quite severe to a carbon-proof deposit, it deposits carbon compulsorily rather here and examines the difference of the carbon-proof deposit nature between the fuel electrode materials at that time. Even if reaction temperature uses which electrode material below 700 degrees C, carbon is not generated so that clearly from drawing 2 , but if 700 degrees C is exceeded, a deposit of carbon will increase rapidly. However, (b) using basic aggregate as electrode material nickel+MgAl<sub>2</sub>O<sub>4</sub>, and (c) nickel+MgO-TiO<sub>2</sub>, (d) nickel+MgO-ZrO<sub>2</sub>, and (e) nickel+CeO<sub>2</sub> All the electrode materials of this invention are understood that the amount of carbon deposits is saturated when 800 degrees C is exceeded. On the other hand also in 800 degrees C or more, as for the conventional (a) nickel+YSZ electrode material, the amount of carbon deposits increased in monotone to temperature. Thus, in the steam reforming reaction of the low S/C ratio, although carbon deposits easily so that high temperature, the carbon deposit was able to be controlled by introducing basic aggregate like this invention. The reaction temperature of 900-1000 degrees C equivalent to especially the operating temperature of SOFC shows that the fuel electrode material of this invention is effective in the carbon-proof deposit nature in internal property modification.

[0029] Drawing 3 and drawing 4 show the scanning electron microscope (SEM) photograph of typical porosity fuel electrode layer / YSZ (electrolyte) base material interface after the end of internal reforming reaction test. The reaction conditions at this time are the temperature of 1000 degrees C, and the conditions as the above with same others. As for the photograph of drawing 3, drawing 4 is the interface of the conventional (a) nickel+YSZ electrode layer and a YSZ electrolyte base material similarly (b) nickel+MgAl<sub>2</sub>O<sub>4</sub>. The interface of a fuel electrode layer is shown, respectively. In respect of a nickel+YSZ fuel electrode boundary, a deposit of about 1-micrometer fibrous carbon is accepted into electrode porosity (whitish portion). However, nickel+MgAl<sub>2</sub>O<sub>4</sub>. In respect of a fuel electrode boundary, such a deposit is not accepted at all and it turns out that the fresh porosity structure in front of property modification is maintained. Drawing 5 - 7 are the SEM photographs when observing fibrous carbon with the large magnification of x10000, x20000, and x35000 accepted in the porosity of said nickel+YSZ fuel electrode by reference. It turns out that the cluster is nuclear-growth-formed for the fibrous carbon in part based on nickel electrode grains. Although a deposit of this carbon fiber is still a stage in early stages of growth, deterioration of the property modification activity which loses the activity surface of nickel gradually and mentions it later in connection with reaction time, and electrode process nature will be urged to it.

[0030] (Fuel electrode process nature examination) In order to evaluate the fuel electrode process nature at the time of the internal property modification of a fuel cell, a cell like drawing 8 was produced by said example of manufacture here. That is, it consists of 3 terminal structures where formed the air electrode 9 and the fuel electrode (nickel+YSZ) 7 in both sides of the solid electrolyte (YSZ) 6, and formed the reforming layer 8 on the fuel electrode 7 further, and the reference electrode 10 was attached to electrolytic [ some ]. In addition, atmospheric interference electrode material used Pt here, although conductive PEROPUSUKAITO type multiple oxide material (LaMnO<sub>3</sub> etc.) was generally used. This is for dissociating with an air electrode and the describing [ above ] 3 terminal method estimating a fuel electrode characteristic, and does not receive the influence in particular by the quality of the material by the side of a counter electrode. Pt was used for the reference electrode and the atmosphere was always held like the inside of the air to it.

[0031] In drawing 9 and drawing 10, it is CH<sub>4</sub>. The electric current-electric potential characteristics of the fuel electrode when supplying steam by S/C=1 (100 cc/min) were shown. The electrode potential of a horizontal axis is the relative electric potential between a fuel electrode and a reference electrode, therefore is equivalent to the balanced electromotive force in the single cell of a fuel cell in the state at the time (electric current =0) of no-load (a figure-0.9V). This electromotive force was not based on a fuel electrode material, but was almost constant and in agreement with the value acquired by the static reaction constant of H<sub>2</sub> / CO/CO<sub>2</sub> / H<sub>2</sub>O gas generated by the steam reforming reaction. Drawing 9 showed the independent characteristics of each fuel electrode material. The highest current density is conventionally obtained with a nickel+YSZ fuel electrode (a), and it turns out that the overvoltage Ross (IR Ross, such as an electrolyte, is almost equal also to each cell) is the lowest so that clearly from a figure. Electrode potential becomes high and a cell's own output also increases, so that overvoltage Ross is low. Among these, it is MgAl<sub>2</sub>O<sub>4</sub> as basic electrode aggregate. (b) and MgO-TiO<sub>2</sub>. The fuel electrode using (c) is obtained only conventional about 1 / about two current density. This is the performance side of a fuel electrode and a previous operation principle shows that the conventional nickel+YSZ fuel electrode is very advantageous. However, in the fuel electrode (f) by the two-layer structure of this

invention, (g), (h), and (i), as shown in drawing 10 , an electrode characteristic equivalent to the former is acquired by installing a nickel+YSZ electrode in the 1st layer, and it turns out that the previous problem was fully solved.

[0032] (Deterioration test of fuel electrode potential with the passage of time) Drawing 11 is the result of actually comparing about deterioration of the fuel electrode potential under fuel cell power generation of internal property modification with the passage of time. The operating condition is the same as the conditions shown by the above-mentioned fuel electrode process nature examination, and the fuel electrode potential is output current density 150mA/cm<sup>2</sup>. It is a value at the time. Although electrode potential was about 0.6v in the early stages of power generation, after that, the conventional nickel+YSZ fuel electrode (a) fell gradually, and, 200 hours afterward, fell to about 0.5v. passing through it with 0.2V, conversely, in the independent fuel electrode (b) using basic aggregate (MgAl<sub>2</sub>O<sub>4</sub>, and MgO and 2TiO<sub>2</sub>), and (c), although electrode potential is low -- the time -- deterioration -- almost -- there is nothing -- things -- understanding . Moreover, MgO-ZrO<sub>2</sub> and CeO<sub>2</sub> Although the independent electrode (d) by aggregate and (e of initial electric potential) are conventionally lower than electric potential, aging is small and, as for the electric potential after 200-hour progress, electric potential rather higher conventionally than an electrode is obtained. The deposit of carbon which showed deterioration of nickel+YSZ electrode performance with the passage of time by previous carbon-proof deposit nature examination is a factor. On the other hand about the two-layer structure fuel electrode (f) of this invention, (g), (h), and (i), the electrode potential obtained by each in early stages of power generation of a nickel+YSZ electrode was maintained stably as it was also even 200 hours after. Thus, highly efficient-ization of the carbon-proof deposit nature at the time of internal property modification and an electrode was solvable at once by adopting the bilayer electrode structure which considered it as the nickel+YSZ electrode at the 1st layer, and used the fuel electrode by this invention as nickel+ basicity aggregate at the 2nd layer.

[0033]

[Effect of the Invention] [ this invention ] by really which made the nickel+YSZ electrode the electrode process active layer, and used nickel+ basicity aggregate electrode as the property modification catalytic activity layer as aforementioned adopting a separation function type two-layer structure electrode It is avoided that a hydrocarbon contacts an electrode process active layer directly, and it can high-activity-ize the electrode process of semi- property modification hydrogen and oxygen ion, and can prevent now deterioration of fuel electrode performance and also fuel cell performance. Moreover, although the S/C ratio was operated in consideration of the measure against a carbon-proof deposit in the conventional internal property modification type power generation 3-4, by using the fuel electrode of this invention, a S/C ratio can be reduced to 1-2, and power generation efficiency can be raised in general from 40 to 45% to 50%. Moreover, in this invention, it can apply also to the fuel cell for the power industries for coal gasification gas, and acts effectively also especially to SO<sub>x</sub>-proof.

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[Translation done.]